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Electronic structure calculations of δ-Pu based alloys

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ABSTRACT

First-principles methods are employed to study the ground-state properties of δ-Pu-based alloys. The calculations show that an alloy component larger than δ-Pu has a stabilizing effect. Detailed calculations have been performed for the δ-$Pu_{1-c}Am_c$ system. Calculated density of Pu-Am alloys agrees well with the experimental data. The paramagnetic → antiferromagnetic transition temperature (T_c) of δ-$Pu_{1-c}Am_c$ alloys is calculated by a Monte-Carlo technique. By introducing Am into the system, one could lower T_c from 548 K (pure Pu) to 372 K ($Pu_{70}Am_{30}$). We also found that, contrary to pure Pu where this transition destabilizes δ-phase, Pu_3Am compound remains stable in the antiferromagnetic phase that correlates with the recent discovery of a Curie-Weiss behavior of δ-$Pu_{1-c}Am_c$ at $c \approx 24$ at. %.

INTRODUCTION

It is strongly believed that many anomalous physical properties of Pu metal, such as many allotropic forms (α, β, γ, δ, δ', and ε), significant (~ 24 %) volume increase for the α → δ transition, negative coefficient of thermal expansion of δ-Pu, low (~ 913 K) melting point, etc., are due to the particular position of Pu in the Periodic Table. In respect to a progressive filling of the 5*f* sub-shell, Pu is located on the border between the light actinides (Th-Np) with itinerant 5*f* electrons and the heavy actinides (Am-Lr) with 5*f* localized states. In other words, the transition from delocalized to localized 5*f* electrons takes place within the plutonium phase diagram resulting in numerous allotropic forms.

Among these phases δ-Pu has received a significant interest in the metallurgical community. This phase is also the most interesting for physicist because its 5*f* electrons exhibit intermediate behavior between delocalization and localization [1]. The δ-Pu phase is stable at temperatures between 593 and 736 K, but can be stabilized at lower temperatures by alloying Pu with a foreign element, so called 'δ-stabilizer'. Among the elements known as δ-stabilizers only four, Ga, Al, Ce, and Am, allow stabilization at and below the room temperature. These stabilizers can be divided into two groups: i) elements with atomic size smaller than the size of the δ-Pu atoms (Ga and Al) and ii) elements with atomic size larger than that of the δ-Pu atoms (Ce and Am).

Recent progress in *ab initio* description of δ-Pu has been made within density functional theory (DFT) that allows for magnetic interactions [2-6]. At elevated temperatures δ-Pu is argued to be a disordered magnet that upon cooling undergoes transformation to an antiferromagnetic (AF) structure ($L1_0$ or type I) with a mechanical destabilization and phase transition to a lower symmetry phase as the result [3, 4]. The calculated [5] transition temperature is in good agreement with temperature measured at the γ → δ transition in Pu. Finally, the lattice constants of Pu_3X ($L1_0$) compounds (X – IIIB metal), recently calculated within the standard spin-polarized KKR-ASA [4] and LAPW [6] techniques, are in excellent agreement with experiment.

In the present study, we mainly concentrated our efforts on the $Pu_{1-c}Am_c$ system where recently an unambiguous Curie-Weiss (CW) behavior has been discovered [7].

COMPUTATIONAL DETAILS

We employ two different computational techniques. First, the scalar-relativistic spin polarized Green function technique based on the KKR method within the multipole-corrected atomic sphere approximation and the muffin-tin correction to the electrostatic energy (KKR-ASA+M) [8, 9]. The other is a full potential linear muffin-tin orbitals (FPLMTO) method [10]. The local Airy gas (LAG) [11] and the generalized gradient (GGA) approximations [12] have been used for the exchange-correlation energy in these methods, respectively.

The spin-polarized KKR-ASA+M calculations were performed for AF (type I) and paramagnetic (PM) arrangements of the spins on the Pu-lattice sites. The PM state of δ-Pu was represented by the disordered local moments (DLM) model [13] incorporated within the coherent potential approximation (CPA) [14].

As KKR-ASA+M approximation is not sufficiently accurate to calculate the elastic constants, we applied the FPLMTO method for this purpose.

RESULTS AND DISCUSSION

According to Söderlind [2], the AF ($L1_0$) structure is the zero-temperature, ground-state magnetic configuration of δ-Pu. Recent calculations bySöderlind et al. [3] show that this ground-state AF structure is closely followed by the mechanically stable disordered magnetic state, about 3 mRy higher in energy. The authors came to the conclusions that the spin entropy could favor the disordered magnetic state at higher temperatures. It was also shown [4] that solutes that help retain the disordered state to lower temperatures also stabilize δ-Pu to lower temperatures. Figure 1 shows the energy difference between equilibrium DLM and AF spin configurations of δ-$Pu_{90}X_{10}$ alloys, where X = Sc, In, Ce, Tl, Am, Cm, Th, and Ac represents the elements with a size exceeding that of δ-Pu (group I), and X = Ni, Co, Fe, Mn, Zn, Ga, Al, and Zr represent elements with a size smaller that of δ-Pu (group II). Notice that doping Pu with a large solute atom lowers the total energy of the DLM phase with respect to the AF phase and thereby stabilizes δ-Pu to lower temperatures. On the other hand, we found that the magnetic 3*d* transition metals from group II (Mn, Fe, and Co) strongly destabilize δ-Pu, in agreement with their experimental phase diagrams.

The calculations in Ref. [4] were restricted to $Pu_{90}X_{10}$ alloys only. In this paper, however, we study $Pu_{1-c}Am_c$ alloys with concentration of Am up to 30 at. %. The DLM → AF transition temperature was obtained from Monte Carlo (MC) simulations within the Ising-type Hamiltonian with the effective cluster interactions (ECI). These were extracted through the Connolly-Williams structure inverse procedure for each $Pu_{1-c}Am_c$ alloy under consideration. The calculations of the ECI have been carried out for the theoretical (DLM) equilibrium lattice parameter defined for all alloys within KKR-ASA+M formalism.

In Figure 2, we show the total energy per atom and its temperature derivative in the MC simulations of pure δ-Pu [5]. The first order phase transition occurs at $T_c \approx 548$ K, which is in fair agreement with the experimental temperature of δ-γ phase transition in Pu (593 K).

Results of MC calculations of the DLM → AF transition temperature in the $Pu_{1-c}Am_c$ system are shown in Figure 3. By introducing Am into the system, the transition decreases from ≈ 548 K

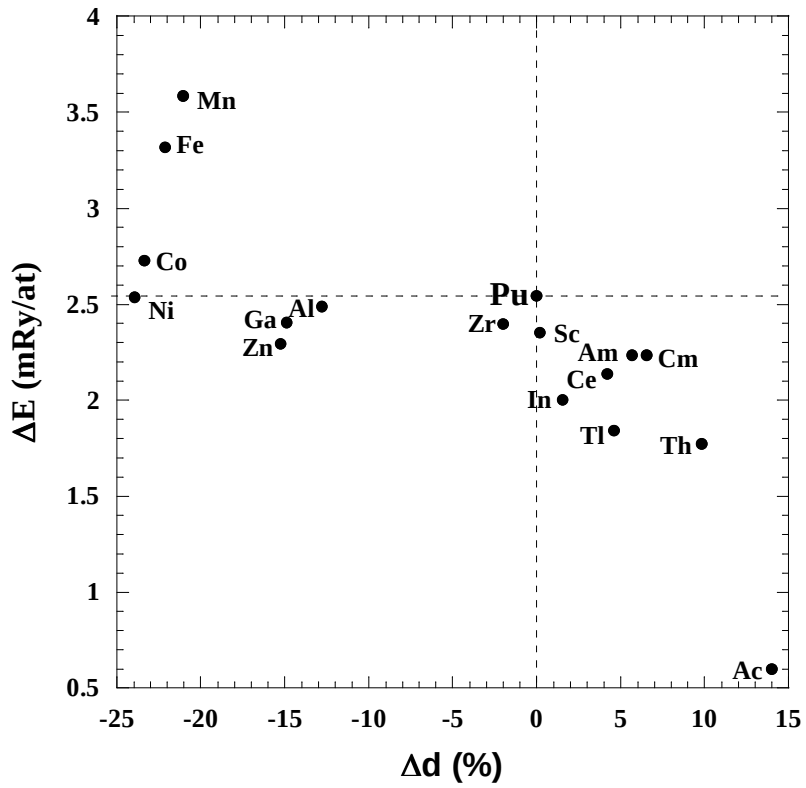

Figure 1. The energy difference between equilibrium DLM and AF configurations of δ-$Pu_{90}X_{10}$ alloys as a function of the difference in Wigner-Seitz radius (Δd) between the components [4].

(pure Pu) to ≈ 372 K ($Pu_{70}Am_{30}$).

Figure 4 shows the calculated and experimental values of the lattice parameter for δ-$Pu_{1-c}Am_c$ alloys. The experimental atomic volumes for this alloy are consistently larger than suggested by the Vegard's law. As could be seen from Figure 4, magnetic calculations are able to reproduce this trend very well. From pure δ-Pu to δ-$Pu_{80}Am_{20}$ alloys, calculations with DLM are shown, whereas beyond that, from δ-$Pu_{75}Am_{25}$ to pure Am, an AF order is applied. This is in accordance with our belief that for δ-Pu alloys with more than ~ 25 at. % Am AF order is preferred at or below room temperature.

Notice in Figure 3 that $Pu_{75}Am_{25}$ alloy is AF at and below ~ 400 K, whereas above this temperature disordered magnetism is expected. As was mentioned earlier, similar magnetic transition occurs also for pure δ-Pu, but at a considerably higher temperature (~ 548 K). In the case of δ-Pu the magnetic DLM → AF transition drives the $\delta \rightarrow \gamma$ phase transition due to a structural instability of the AF phase. For Pu-Am alloy, however, no such structural phase transition has been found suggesting that the AF configuration remains mechanically stable. Theoretically, this hypothesis can be corroborated by calculating elastic constants or relevant deformation energies for the AF Pu-Am alloy.

The $Pu_{75}Am_{25}$ alloy was modeled by a Pu_3Am ($L1_2$ structure) compound when calculating deformation energies using the FPLMTO method. In Figure 5 we show relative energies for AF Pu_3Am and AF δ-Pu as a function of *c/a* axial ratio. Notice that for δ-Pu the AF configuration is strongly unstable with respect to the tetragonal distortion, whereas the Pu_3Am system remains mechanically stable, with a minimum in the total energy for *c/a* = 1.414. Hence, there is a

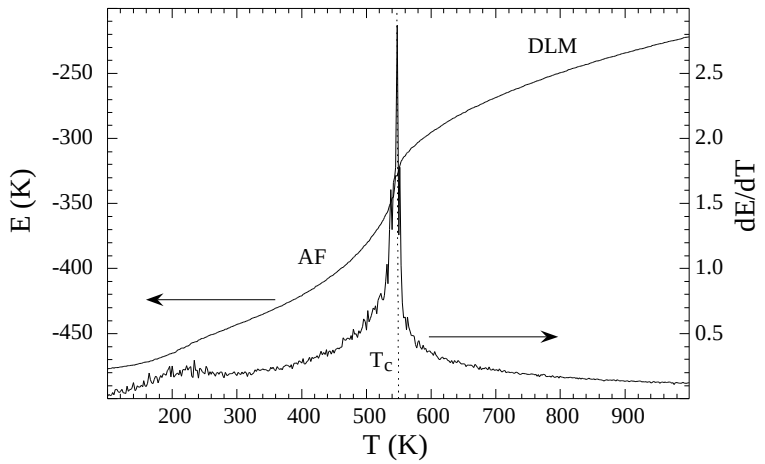

Figure 2. The configurational energy per atom E (K*)* and its first temperature derivative (dE/dT) as a function of temperature in the Monte Carlo simulations of δ-Pu.

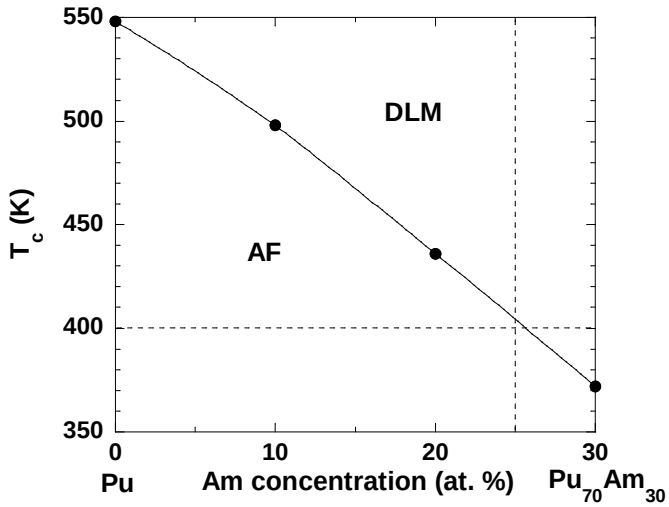

Figure 3. DLM → AF transition temperature for δ-$Pu_{1-c}Am_c$ alloys.

fundamental difference between δ-Pu and Pu_3Am in that while both undergo a magnetic DLM → AF transition, it destabilizes δ-Pu but not the Pu_3Am compound. This is important because our theory thus predicts the possibility for an AF order in the Pu-Am system. Our theoretical picture, indeed, is in a good agreement with recent measurements of the magnetic susceptibility in the Pu-Am system where, at ≈ 24-26 at. % Am, CW behavior has been discovered [7].

It is well known that Pu and other actinides with itinerant 5*f* states tend to crystallize in low symmetry and open structures and that the reason for this is due to high density of 5*f* states at the Fermi level (E_F) that efficiently rules out high symmetry structures [16]. It is tempting to associate the destabilization of AFδ-Pu at low temperatures to a similar phenomenon. We therefore show, in Figure 6, the calculated (FPLMTO) electronic density of states (DOS) for AF Pu and Pu_3Am. This plot focuses on the DOS behavior in the vicinity of the E_F. Notice that for pure Pu, there is a strong peak intersecting the E_F with its maximum just below. This is an inherently unfavorable situation due to the large contribution of this peak to the band energy [16]. For Pu_3Am, however, this peak is shifted mostly below E_F, which is now located close to a

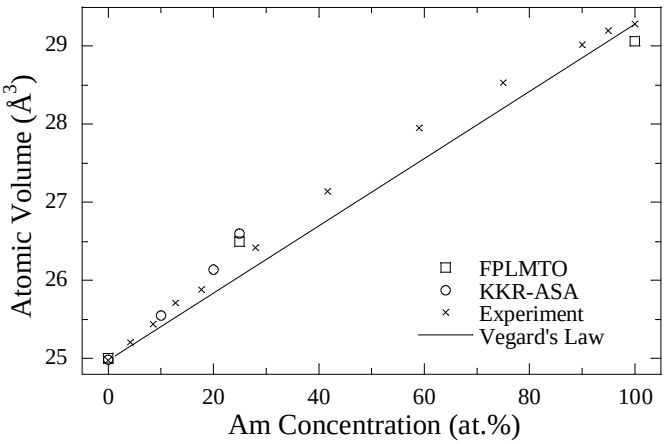

Figure 4. Lattice parameter for δ-Pu-Am alloys. Experimental data are taken from Ref. [15].

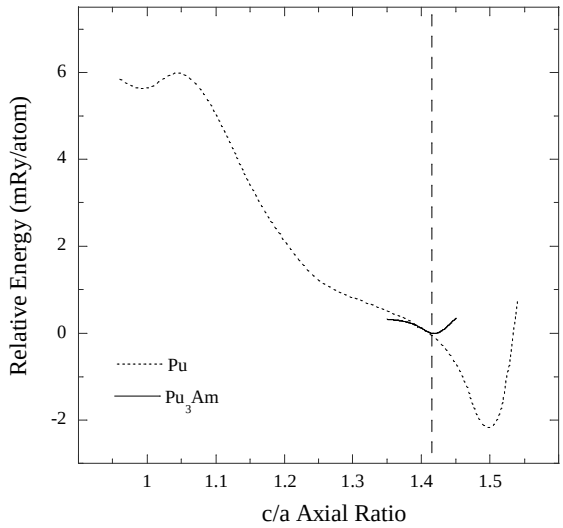

Figure 5. Relative energy as a function of *c/a* axial ratio for Pu and Pu_3Am in mRy/atom.

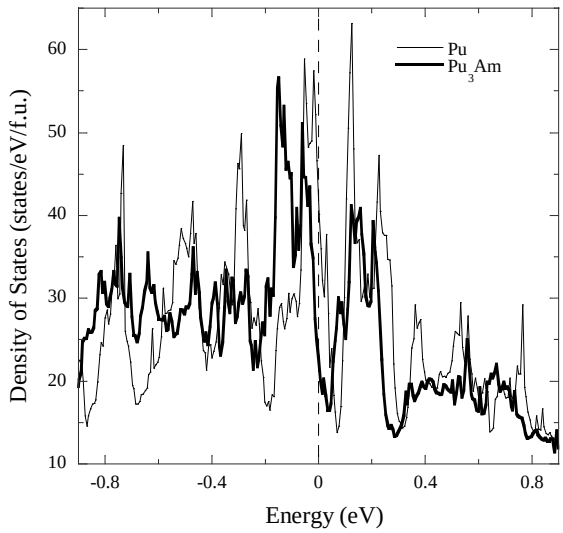

Figure 6. Total electronic density of states for Pu and Pu_3Am in states/eV/f.u. The energy scale is shifted so that the Fermi level is positioned at zero energy.

minimum in the DOS. This shift of the E_F in Pu_3Am relative to pure Pu is a consequence of the additional 5*f* electrons provided by the americium in this compound. We speculate that this more stable situation in Pu_3Am is responsible for the mechanical stability in this system.

CONCLUSIONS

We have studied the δ-Pu-Am system theoretically by means of density -functional electronic-structure techniques. The question of antiferromagnetism has been addressed first by studying a possible magnetic transition in the Pu-Am alloy with 25 at.% Am content. MC simulations within the Ising model predict this alloy to be AF below about 400 K. In addition, calculations suggest that AF order is mechanically stable for this alloy, further supporting its existence. Details of the electronic structure show that the additional 5*f* electrons provided by the Am shifts the Fermi level to a more stable position in the electronic density of states that may explain the stabilization of the Pu-Am alloy.

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